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A STUDY OF SCIENTIFIC RESEARCH MATERIALS

FINAL REPORT

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MATERIALS RESEARCH
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ORANGEBURG, NEW YORK

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A STUDY OF SCIENTIFIC RESEARCH MATERIALS

FINAL REPORT

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Orangeburg, New York

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	
PART I	
- (1) ABSTRACTS OF PAPERS PUBLISHED:	
Parameters Pertinent to the Electron Beam Zone Refinement of Refractory Metals;.....	1
Age-Hardening in a Gold-Nickel Alloy;.....	2
The Preparation and Properties of the Intermediate Phase Based on the Compound TiCo;.....	6
The Effect of Ultra-High Vacuum Electron Beam Zone Refining on the Purification of Metals;.....	7
The Relation Between Vacuum and Purity in Float-Zone Melting of Refractory Metals,.....	8
PART II	
- (2) COMPLETED WORK TO BE SUBMITTED FOR PUBLICATION:	
Electron Beam Heating of Ceramic Materials;.....	1
Phase Relationships in the Ti-Co System;.....	20
PART III	
- (3) UNPUBLISHED WORK:	
Preparation of Volatile Compounds;.....	1
Preparation of a Cadmium-Alumina-Silica Glass;.....	10
Characterization by Field Ion Microscopy;.....	19
Electrotransport as a Means of Purification;.....	21
Characterization of Ni ₃ Al.	

INTRODUCTION

The original objectives of the work performed on Contract No. AF 49(638)-1241 were to develop new and improved techniques for the synthesis, purification and crystal growth of research materials. In an attempt to focus attention on a more specifically defined area, the work was to be conducted on materials that possessed melting points above 1000°C. Towards this end the work was confined to refractory metals, intermetallic compounds, equiatomic alloys, and certain ceramic materials.

This final report is separated into three parts. In the first part published work is presented in abstract form. Since this work has been previously submitted to ARPA in detailed form and since the papers have now appeared in the literature, it was thought that its inclusion herein would be only unnecessary repetition. In the second part of this report work is presented that has now been prepared for publication but has not been previously submitted to ARPA. These papers are included in final and completed form. In the third part work is discussed that has either not been carried to finalization or was not of a publishable nature. This work also will be reported here in detail.

PART I

ABSTRACTS OF PAPERS PUBLISHED

Title: PARAMETERS PERTINENT TO THE ELECTRON BEAM ZONE
REFINEMENT OF REFRactory METALS

Authors: I. Drangel and G. T. Murray

Presented: at AIME Refractory Metal Symposium, New York, 1964.

Published: by Gordon and Breach, New York, 1965.

A study has been made of the effect of several processing parameters on the resulting purity of electron beam refined molybdenum and tungsten. Resistance ratio measurements, i.e. $R_{298^\circ K}/R_{4.2^\circ K}$, have been used to evaluate the material.

It has been found that purification of molybdenum and tungsten in the electron beam float-zone refining process occurs primarily by volatilization of gaseous elements and compounds and by vacuum distillation of the lower melting point elements. The degree of purification is quite dependent on the extent to which these products can be removed by the vacuum system. After about five zone passes at a zoning speed of 9"/hour purification by zone melting per se commences near the starting end. Resistance ratios as high as 70,000 and 14,000 have been achieved on tungsten and molybdenum respectively. The molybdenum could be deformed by swaging to 99.9% R.A. and the tungsten to 15% R.A. at room temperature.

Title: AGE-HARDENING IN A GOLD-NICKEL ALLOY
Authors: A.A. Johnson, E.J. Hughes, P.W. Barton
Published: as a Letter to the Editor, Nature, Vol. 201, No. 4923, pp. 1020-1021, March 7, 1964.

One factor which may limit the mechanical strength which can be achieved in a conventional age-hardening alloy is the volume fraction of the alloy which can separate out as a precipitate. This is determined by the change in solute solubility in going from room temperature to the highest possible solution treatment temperature, that is, to the solidus temperature. There is, however, a small class of alloy systems (gold-nickel, gold-platinum and chromium-tungsten) to which this limitation does not apply. In these systems complete miscibility occurs at high temperatures, but at lower temperatures there is a miscibility gap. Although precipitation phenomena occurring in these systems in alloys of high solute concentration have to some extent been studied (for example, refs. 1-5), the accompanying age-hardening effects have been almost totally neglected. The purpose of this communication is to report the results of a preliminary study of age-hardening in an equiatomic gold-nickel alloy.

The alloy was prepared by melting together appropriate amounts of high-purity gold and nickel in a recrystallized alumina crucible under a vacuum of 10^{-5} mm mercury. It was then remelted several times to ensure its homogeneity,

encapsulated in an evacuated quartz tube, solution treated for 1 hr. at 900°C, and quenched into a mixture of ice and water. A rod of the alloy 0.050 in. in diameter was fabricated by rolling and swaging and, from this, tensile specimens having a 3/8 in. gauge length and a 0.030 in. gauge diameter were machined. The machined specimens were then encapsulated individually, solution treated for 1 hr. at 900°C, and quenched into a mixture of ice and water. A number of these specimens was annealed for 1 hr., each at a different temperature in the range 100°-900°C, and again quenched into ice and water. These annealed specimens and one solution-treated specimen were then tested at room temperature in an autographically recording hard beam tensometer at a strain rate of $3 \times 10^{-4} \text{ sec}^{-1}$.

Fig. 1 shows the yield stress of each specimen, that is, the stress at which a measurable deviation from Hooke's law could be detected on the load-elongation curve, plotted against annealing temperature. A large hardening peak occurs at about 450°C and a much smaller one at about 150°C. These two peak temperatures fit in well with the results of the earlier precipitation studies on this system¹⁻³. The main peak corresponds to the onset of precipitation and the smaller one to a transient pre-precipitation structure detected by earlier workers using electrical resistivity measurements¹, electron diffraction², and other techniques^{2,3}.

These results represent only a preliminary investigation in which no attempt has been made to optimize the hardening

effects. It is interesting, therefore, that the peak value of the yield stress, achieved by annealing at 450°C, is greater than that of the strongest nickel-base alloy at present available commercially. Precipitation in high solute alloys of this kind, therefore, seems to provide a useful method of alloy hardening which might lead to the development of new engineering materials, especially in the case of the chromium-tungsten system. From this point of view the aluminum-zinc system may also be of interest. Its phase diagram is more complex than those of the three systems discussed here, but it also allows the possibility of studying age-hardening in alloys of equiatomic composition.

This work is being continued and extended to the systems gold-platinum, chromium-tungsten and aluminum-zinc.

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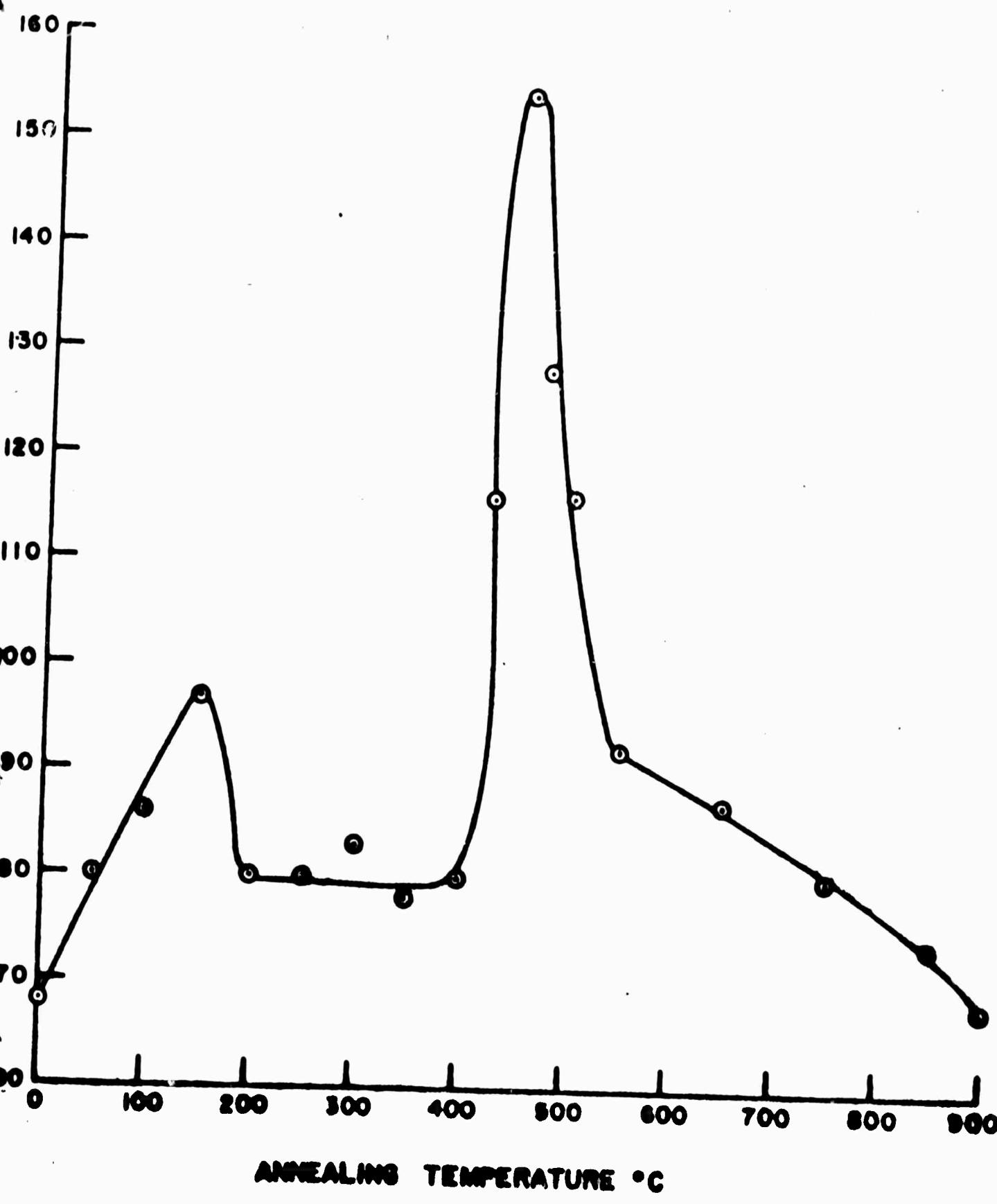


FIG. 1

Title: THE PREPARATION AND PROPERTIES OF THE INTER-MEDIATE PHASE BASED ON THE COMPOUND TiCo

Authors: P.W. Barton, E.J. Hughes and A.A. Johnson

Presented: at the First International Conference on Electron and Ion Beam Science & Technology, Toronto, 1964.

Published: by John Wiley (R. Bakish, ed.) 1965.

The intermediate phase based on the compound TiCo has been shown to exist at room temperature in equilibrated and slowly cooled specimens over a range of compositions from about 49.5 to 54.5 at% cobalt. A technique is described for preparing rods of single phase material by arc-melting under purified argon followed by electron beam zone melting.

Measurements are reported of its tensile properties between room temperature and 750°C, electrical resistivity between -269° and 86°C, oxidation rate in air up to 900°C, and corrosion rates in a series of liquid environments at 80°C.

Title: THE EFFECT OF ULTRA-HIGH VACUUM ELECTRON BEAM ZONE REFINING ON THE PURIFICATION OF METALS

Authors: I. Drangel, P. McMahon and S. Weinig

Presented: at Sixth Alloyd Electron Beam Symposium, April 1964.

To be published.

Previous results of work performed using conventional electron beam zone melters with vacuums in the range of 10^{-5} to 10^{-7} torr indicated that significantly greater purities in metals might be achieved by operating at lower chamber pressures. An apparatus was designed and constructed for zone melting in an operating vacuum of 10^{-9} torr in order to investigate further this effect on the purification of metals.

The principles of the electron beam float-zone melter were incorporated into an all stainless steel bakeable chamber. This system includes both external and internal bakeout units to facilitate achieving the desired operating vacuums.

The parameters used for the evaluation of materials were resistivity ratios as a measure of impurity levels and microhardness and fabricability at room temperatures as a measure of mechanical properties. Preliminary results on the metals tungsten and molybdenum are indicated. The effects of heat treatments on the measured resistivity ratios for molybdenum are discussed.

Title: THE RELATION BETWEEN VACUUM AND PURITY IN
FLOAT-ZONE MELTING OF REFRACTORY METALS

Authors: G.T. Murray, S. Weinig and I. Drangel

Presented: at the June 1964 Vacuum Metallurgy Society,
New York.

Published: Vacuum Metallurgy Transactions, Am. Vac. Soc.
1964.

Molybdenum and tungsten have been float-zone melted at pressures varying from 10^{-4} to 10^{-8} torr utilizing three different electron beam refiners. The resulting resistance ratio measurements showed a continuous increase in value as the degree of vacuum was increased. For tungsten the resistance ratio after only one zone pass in the 10^{-8} system exceeded 30,000 compared to 3,300 for one pass in the 10^{-4} system.

For the larger diameter rods it was apparent that solute diffusion in the liquid state was the rate controlling factor. By the introduction of mechanical agitation of the melt via rotation of one section of the rod being zoned, it was possible to eliminate the dependency of purity on the specimen size. In this manner 1/4" diameter molybdenum was obtained which possessed a resistance ratio of 12,000. This value is comparable to that obtained on 1/8" diameter specimens without the benefit of specimen rotation. This material was found to be extremely ductile being capable of 99.9% R.A. at room temperature without any evidence of fracture.

An analysis of the effect of vacuum purification indicates that its major influences are:

- a) The better removal of gaseous products via faster pumping speeds.
- b) The reduction in gas solubility in the liquid phase by reduction of the partial pressure in the gaseous phase.
- c) The minimization of recontamination on the hot solid sections of the rods being zoned.

PART II

COMPLETED WORK TO BE SUBMITTED FOR PUBLICATION

ELECTRON BEAM HEATING OF CERAMIC MATERIALS

INTRODUCTION

During the past decade electron beam heating has been successfully used for melting a wide variety of metals and alloys. Its application to purification of metals by float-zone refinement has been recently reviewed by Schadler (1) and by Lawley (2). Less attention, however, has been paid to its application to processing of compound materials. The lack of interest in the electron beam melting of compounds is due to the existence of several additional complex phenomena that are not present in the melting of metals. Firstly, many compounds possess electrical conductivities that are too low to permit melting by the conventional work-accelerated process. Secondly, many compounds tend to decompose on melting, unless a suitable atmosphere of the more volatile constituent is provided. These compounds are not suited to the vacuum electron beam process. Finally, some compounds melt incongruently, that is, the solid compound dissociates to form a new solid phase and a liquid of different composition. Many of these compounds are not suited to preparation by any type of melting operation and usually must be formed by sintering powder compacts.

The first of these difficulties, i.e. the lack

of electrical conductivity can be circumvented by a grid technique (to be described later). The compounds that melt incongruently must be processed by other techniques. The problem of decomposition in vacuum remains to be considered. Here one can make some qualitative predictions from thermochemical data as to the relative stability of various classes of compounds. In order to evaluate the stability of compounds in the molten state, one needs some measure of the bond strength in this state. Unfortunately, data on actual bond strengths are not available. The only data that is available that indicates to some extent the stability and bond strength of a compound is the standard free energy of formation. In Figure 1 the free energy of formation as a function of temperature has been plotted for a number of the more common oxides, nitrides and carbides. The data compilation of Wicks and Block (3) were used here and extrapolated to the melting point. Based on this data it appears that the oxides are more stable than the nitrides and carbides, the latter two falling within the same range of about -10,000 to -50,000 cal./mol./°K.

The free energy of formation at best is only a qualitative measure of the stability of these compounds

in vacuum. The relative vapor pressures of the elements and the compounds in the molten state is also of concern but little quantitative information is available with respect to these parameters.

The object of the present work was to investigate some of the more common nonmetallic compounds and to ascertain which of these would be amenable to preparation by electron beam techniques. The materials studied included carbides, borides and oxides.

EXPERIMENTAL

A. Apparatus

A commercial (MRC Mfg. Corp. Model EBZ-93) electron beam unit was utilized for the present work. This unit has been described in detail by Hurwitt and Adams (4). In essence, it consists of a high capacity vacuum pumping system, a 10KV power supply, an evacuated chamber which contains the scanner assembly and specimen holder, and a control panel containing the scanner speed control, filament and vacuum gauges. The specimen was suspended from the mount such that the float-zone method was attempted in all cases.

In the conventional electron beam float-zone method the specimen is maintained at a high potential relative to the emitter and focusing shields which

are maintained at or near ground potential. This type of operation requires that the specimen be a relatively good conductor. This type of arrangement was used for the carbides and borides but for the insulating oxides it was found necessary to modify this specimen-emitter configuration by the insertion of a high positive potential grid, between the emitter and specimen (Figure 2). A technique of this type was first described by Neumann and Huggins (5) for the melting of Al_2O_3 . In the present work the emitter was still maintained at ground potential while the grid was attached to the high voltage power supply. No potential leads were attached to the specimen. The grid consisted of 0.020 to 0.030" tungsten wire in the form of a helix of about 1/2" in length. The grid acts to accelerate the electrons from the emitter toward the specimen where impingement and melting occurs. In addition it acts to remove the negative charge build-up on the specimen.

B. Materials

Two types of compounds were used in the electron beam zone refiner, namely sintered rods that were obtained from commercial sources, and arc-melted compounds prepared in our own laboratory. In the latter case, elemental powders were mixed in various

proportions, compacted at room temperature, and then melted into long rods in an arc melter. The arc melter consisted of a tungsten electrode, a water cooled copper hearth into which long grooves were machined to hold the starting material, and a 100 amp. power source. After loading the hearth with the starting material, the chamber was evacuated, purged several times with purified argon, and then maintained at about 1/3 atm. pressure of argon during melting. The ingots were melted several times being turned over in the hearth after each fusion operation. The purpose of the arc melting operation is to produce rods that are mechanically stable with respect to subsequent handling and mounting in the electron beam apparatus.

RESULTS

A. Work-Accelerated Beam

1. Carbides

The utility of the electron beam float-zone refiner for processing of relatively low resistivity compounds was demonstrated several years ago both at MRC (6) and by Chang et al at Atomics International (7). In these experiments uranium monocarbide was melted and purified using the work-accel-

erated float-zone technique. Chang et al also obtained single crystal material by this process.

In the present work carbides of Ti, Zr, B, Nb and Ta were investigated, the latter two in some detail. Except for B_4C , all of the carbide starting rods were fabricated by cold pressing mixtures of the elemental powders followed by fusion in the arc furnace.

Arc melted rods prepared from stoichiometric powder mixtures of TiC (m.p. $3250^{\circ}C$) and ZrC (m.p. $3500^{\circ}C$) exhibited almost identical behavior when heated in the electron beam apparatus. As the power was increased to about 5 KV and 200 ma settings, temperatures near the melting points were achieved. However, before fusion could be obtained evaporation became so excessive that the material in the region being heated almost completely disappeared and deposited on the walls of the work chamber. It was concluded that the high vapor pressures of TiC and ZrC prohibited electron beam zone refinement in a dynamic vacuum of 10^{-5} mm Hg.

Boron carbide (B_4C) pressed pellets of $1/4"$ diameter by 1" length were obtained from the Norton Company. These pellets were stacked in the electron

beam apparatus as one continuous rod. At a power level of 3.0 KV and 200 m.a., fusion occurred and a length of about 1/2" was zone melted. However, large quantities of material were vaporized which eventually led to an electrical short and cessation of the run. The molten material was crushed and examined via X-ray diffraction powder patterns. The pattern showed distinct lines of both B_4C and carbon. No attempt was made to quantitatively determine the extent of the carbon loss but it was evident from the diffraction lines that the majority of the sample consisted of the compound B_4C .

Preliminary electron beam experiments with arc melted rods of NbC and TaC showed that this material could be easily zone melted. Although some vaporization occurred, lengths of several inches could be zone melted without the occurrence of either electrical shorts or excessive loss of material. Chemical analyses also showed that carbon evaporated preferentially and that the composition of the starting mixture must be adjusted to compensate for this loss. Consequently a series of powder mixtures of varying composition were arc melted and then zone melted in the electron beam apparatus. These samples were examined metallographically, chemically, and by X-Ray diffraction

(all tests were not performed on all samples). The results obtained are listed in Tables I and II.

For tantalum-carbide mixtures, the carbon loss was relatively small during arc melting and single phase material was easily attained. The compound TaC varies in composition from about 4.9 to 6.3 weight per cent carbon. The X-ray and metallographic results on all samples examined showed that TaC only was obtained on arc melting, even when a large excess carbon was added. However, considerable carbon loss was observed during beam melting resulting in mixtures of two or more phases.

The niobium-carbide results were somewhat better with respect to beam melting. In one case a single phase was obtained throughout the specimen and in other cases large regions of single phase material resulted. The carbon-deficient region was always near the outer surface.

2. Borides

Hot pressed TiB_2 rods of 0.25" diameter and about 3" length were obtained from the National Carbon Company. Several attempts were made to melt these rods in the electron beam unit at pressures varying from 10^{-5} to 10^{-6} mm Hg. Complete fusion was never achieved. Instead the rods appeared to decompose or

vaporize at temperatures below the melting point (2200°C).

B. Grid Technique - Oxides

The grid technique described earlier was employed for all oxides examined. The type of material investigated and the behavior observed on heating in the electron beam are listed in Table III. For these tests the vacuum employed in all cases was between 10^{-5} and 10^{-6} mm Hg.

Al_2O_3 was easily zone melted over lengths of several inches. For this material the bottom sections of the rods were rotated at about 200 rpm during the zoning operation to ensure that complete melting was being achieved and also to enhance purification. In the $1/8"$ diameter rod single crystals of several inches in length were obtained from both the Morganite recrystallized material and the Linde Sapphire single crystal rod. It was not determined whether or not the as-received orientation of the sapphire crystal was maintained. The $1/4"$ diameter rod was also zone melted over long lengths but in this case single crystals were achieved only over very short ($\sim 1'$) sections. It appeared that the change from the single to the polycrystalline mode of growth was a result of crack formation via thermal stress gradients.

Samples of the zone melted Morganite material were sent to the National Research Corporation for spectrographic analyses. The results are compared to that of the starting material in Table IV. For the Morganite material some purification was achieved except for the element silicon which was reported as 500 ppm in one zone refined sample, but was not checked in the other specimen. This is believed to be an error in analysis since silicon pick-up was not found after zone melting the Linde material. The latter, which was very low in initial solute, showed essentially no change on zone refining (most elements were below the detectable limit of the emission spectrograph). It has been previously demonstrated (8) that in the electron beam refinement of metals, purification occurs primarily by volatilization of the gaseous elements (and compounds such as CO_2) and by vacuum distillation of the lower melting components. The major impurities in the as-received Morganite material consisted of the oxides of silicon, iron, sodium and potassium. The oxides of sodium and potassium possess melting and sublimation points far below that of Al_2O_3 and thus should be easily removed. The analyses show this to be true.

Fe_2O_3 possesses a melting point of 1565°C or about 500°C below that of Al_2O_3 . Considerable purification with respect to iron content was achieved.

SiO_2 melts in the vicinity of 1700°C . Based on this criterion alone one would expect some purification with respect to the silicon content. Such was not observed. If the vapor pressure of SiO_2 were similar to that of Al_2O_3 at the melting temperature, purification by vacuum distillation would not be expected. Unfortunately, this data is not available.

The results of the experiments conducted on the remaining oxides were much more difficult to interpret. Only in the case of UO_2 was fusion clearly established. Decomposition was evident for ZrO_2 and MgO . The reason for these uncertainties in some cases was due to the porous nature of the starting material. Whereas the Al_2O_3 used in the present work was near theoretical density, the density of the other oxides varied from 68% for ZrO_2 to 90% for TiO_2 of theoretical density. When such a porous material is heated in vacuum, excessive gas evolution causes electrical shorts to the emitter in some cases and in others causes spalling and flaking of the rod. At first glance one tends to interpret this occurrence as sublimation or decomposition. That this was not

always the case was proven by heating a very porous Al_2O_3 rod. In this material fusion was never achieved, rather the rod spalled and flaked much similar to that observed for most of the other oxides.

Based on the free energy of formation data of Figure 1, one would expect that of the compounds examined, Al_2O_3 would be the least likely to decompose in vacuum and such was the experimental observation. However, UO_2 , ZrO_2 and ThO_2 also possess relatively large negative free energies of formation. Of these three, UO_2 at the moment shows the most promise of being amenable to electron beam zone refinement. The ZrO_2 used was the calcium stabilized variety and this may account for its decomposition. Before definite conclusions can be made on ThO_2 and ZrO_2 , experiments must be conducted on higher density starting material.

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TABLE I

RESULTS OF ARC-MELTED AND BEAM-MELTED
TANTALUM CARBIDE SPECIMENS

Mixture Composition (wt % Carbon)	AS ARC-MELTED			AFTER ELECTRON-BEAM MELTING		
	Chemical Analysis % Carbon	Metallography	X-Ray	Chemical Analysis	Metallography	X-Ray
6.23	5.37	Single Phase	TaC	---	2 Phases	TaC+Ta ₂ C
6.8	5.17	Single Phase	---	2.43	2 Phases	---
5.8	---	---	---	---	Ta ₂ C+Eutectic	---
12.6	---	Single Phase	TaC	3.03	TaC+Eutectic	TaC,Ta ₂ C,Ta

TABLE II

RESULTS OF ARC-MELTED AND BEAM-MELTED
NIOBIUM-CARBON SPECIMENS

Mixture Composition wt % Carbon	AS ARC-MELTED			ELECTRON-BEAM MELTED		
	Chemical Analyses	Metallography	X-Ray Results	Chemical Composition	Metallography	X-Ray Results
11.45	---	Single Phase	NbC	10.53	2 Phases	NbC+Nb ₂ C
12.0	9.92	---	---	8.42	2 Phases (One region of single phase)	NbC+Nb ₂ C
12.0	---	---	---	---	Single Phase	---
12.5	---	---	---	---	2 Phases	---
18.0	---	Eutectic	NbC+C	7.72	Three Regions center-Eutectic middle-NbC outside-NbC+ Nb ₂ C	NbC+Nb ₂ C +C

TABLE III
ELECTRON BEAM PROCESSING OF OXIDES

Material	Type	Beam KV	Power ma	Results
Al_2O_3	1/8" dia. Morganite recrystallized rods	1.5	160	Molten zone easily maintained, single crystals obtained.
Al_2O_3	1/4" dia. Morganite recrystallized rods	3.0	195	" " " "
Al_2O_3	1/8" Linde Sapphire crystals	3.0	180	" " " "
Al_2O_3	1/4" Linde Sapphire crystals	3.5	200	" " " "
MgO	1/4" sintered rods	--	--	Decomposed prior to melting
ZrO_2	1/4" sintered stabilized rods - Norton Company	3.5	200	Decomposed.
UO_2	3/8" pressed rods	2.2	70	Gas evolved - some melting occurred, decomposition uncertain.
ThO_2	1/4" dia. sintered rods, Zirconium Corp.	1.5	100	Gas evolved - Decomposition uncertain
TiO_2	Powder - packed in Al_2O_3 crucible	2.2	100	Oxygen evolved - some fusion, air anneal restored stoichiometry.

TABLE IV

ANALYSES* OF ZONE-MELTED Al_2O_3

Material	Weight ppm															
	Fe	Cr	Ni	Cu	Ti	Mn	Mg	Si	B	Sn	Pb	Na	K	V	Mo	W
Morganite	50	10	10	8	15	7	7	100	<50	ND						
Starting Material										<10	<30	70	10	--	--	--
3 Pass beam refined	0	ND <10	ND <10	1	20	1	5	500	<50	ND	ND	<30	10	5	ND	ND
										<10	<10	<10	<10	<10	<10	<10

* Avg. of 2 specimens

ND - Not Detectable

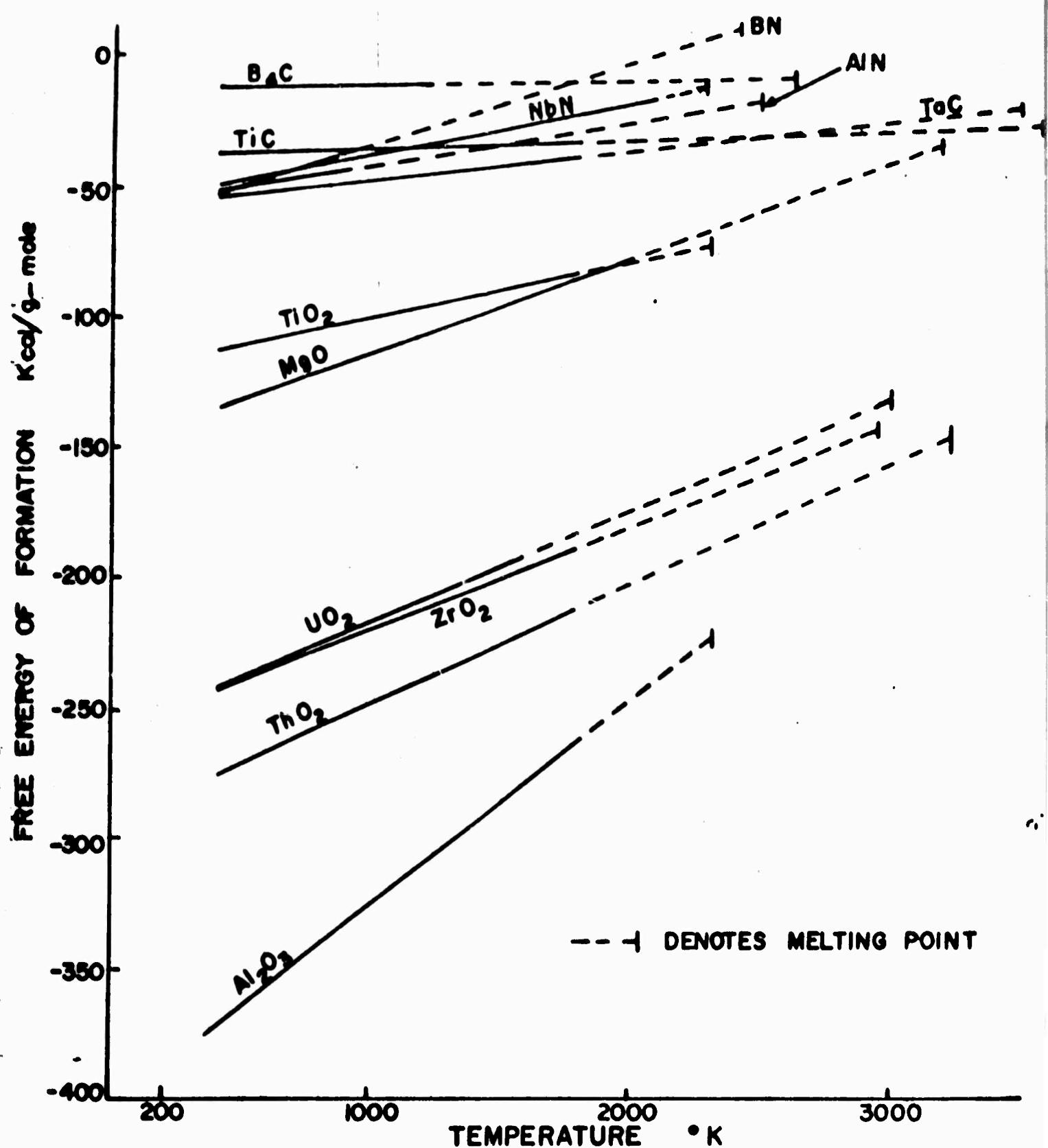


FIGURE 1 FREE ENERGY OF FORMATION VERSUS TEMPERATURE

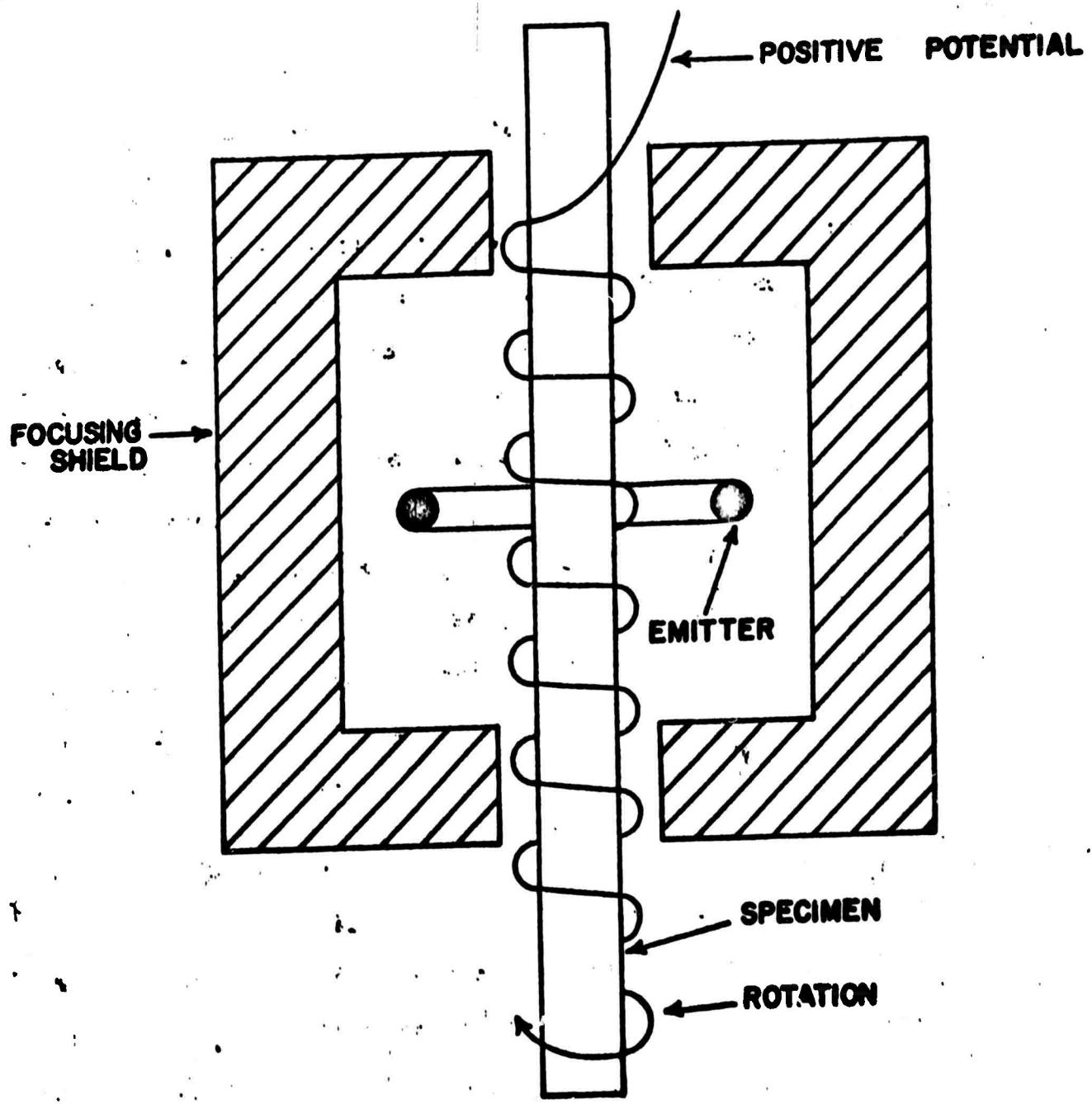


FIGURE 2 ZONE MELTING OF INSULATORS

PHASE RELATIONSHIPS IN THE Ti-Co SYSTEM

INTRODUCTION

In the course of previous work (1) on the preparation of the Ti-Co intermetallic compound, it was found that accurate phase relations near the stoichiometric composition were unknown. Work on the Ti-Co system which has been summarized by Hansen and Anderko (2), revealed the existence of three compounds, namely Ti_2Co , $TiCo$, and $TiCo_2$. Although earlier workers showed that the structure of the $TiCo$ compound was body-centered cubic the phase boundaries were not established. Consequently it was decided to redetermine this region of the phase diagram using high temperature x-ray diffraction techniques.

EXPERIMENTAL

A series of alloys varying in nominal composition from 46 to 55 atomic percent was prepared by arc melting beam refined materials in a purified argon atmosphere. During the melting process stirring of the melt sufficient to eliminate the need of a further homogenization anneal was accomplished. As a check, all specimens were examined metallographically and found to be homogeneous. Alloys were sent out for analysis of the actual Ti and Co content as well as impurity content. The specimens were annealed at $1000^{\circ}C$ for $1\frac{1}{4}$ hours to achieve equilibrium. The cooling rate was controlled so that the specimens were cooled to

500°C in about 2 hours. The power was then turned off and specimens allowed to cool to room temperature. The cobalt rich specimens were given a further equilibrium anneal at 1130°C for 24 hours and again allowed to cool slowly.

Samples from each alloy prepared were selected for x-ray studies. They were crushed, ground to 325 mesh, then further annealed in vacuum at 1000°C for 30 minutes to remove any cold work introduced by the grinding operation. A high temperature diffractometer attachment (MRC Model X-86N-II) was utilized for the x-ray diffraction studies. This attachment was mounted directly onto a Norelco Goniometer and x-ray patterns obtained over a wide range of temperatures.

In this investigation a thin layer of each composition was placed on the diffractometer stage. The layer was kept thin in order to avoid possible temperature gradients throughout the specimen. A diffractometer trace was made at room temperature and, without disturbing the specimen, a scan was made at each of the temperature intervals represented by the points in Figure 1. The use of only one small sample from each composition over the entire temperature range greatly simplified the procedure. The temperature intervals were 100°C at the lower temperatures and 50°C at temperatures above 800°C. Power was supplied from a unit that is capable of furnishing 0 to 80 amperes at 0 to 5 volts. The sample

was allowed to equilibrate at each temperature for 1/2 hour. All diffractometer traces were obtained while the specimens were under a vacuum of 5×10^{-6} mm Hg.

RESULTS

The analysis of the x-ray diffraction data is depicted in Figure 1. The single phase region for the compound TiCo was found to extend from about 45 at% Ti to 51 at% Ti. This information has been combined with existing data (2) to show a complete phase diagram for the titanium-cobalt system (Figure 2). From the large number of samples investigated and the sensitivity of the measurements, it is believed that the data in Figure 1 represent a precise determination of the phase boundaries for the TiCo region of the diagram. Note that the samples for the points near the left phase boundary were separated in composition by only 0.6 at%. Yet the diffraction patterns clearly showed the difference between the two phase and single phase regions. Likewise with respect to the high titanium content boundary, samples separated in temperature by 100°C distinguished the single and two phase samples. Work on the solidus and liquidus region is still in progress.

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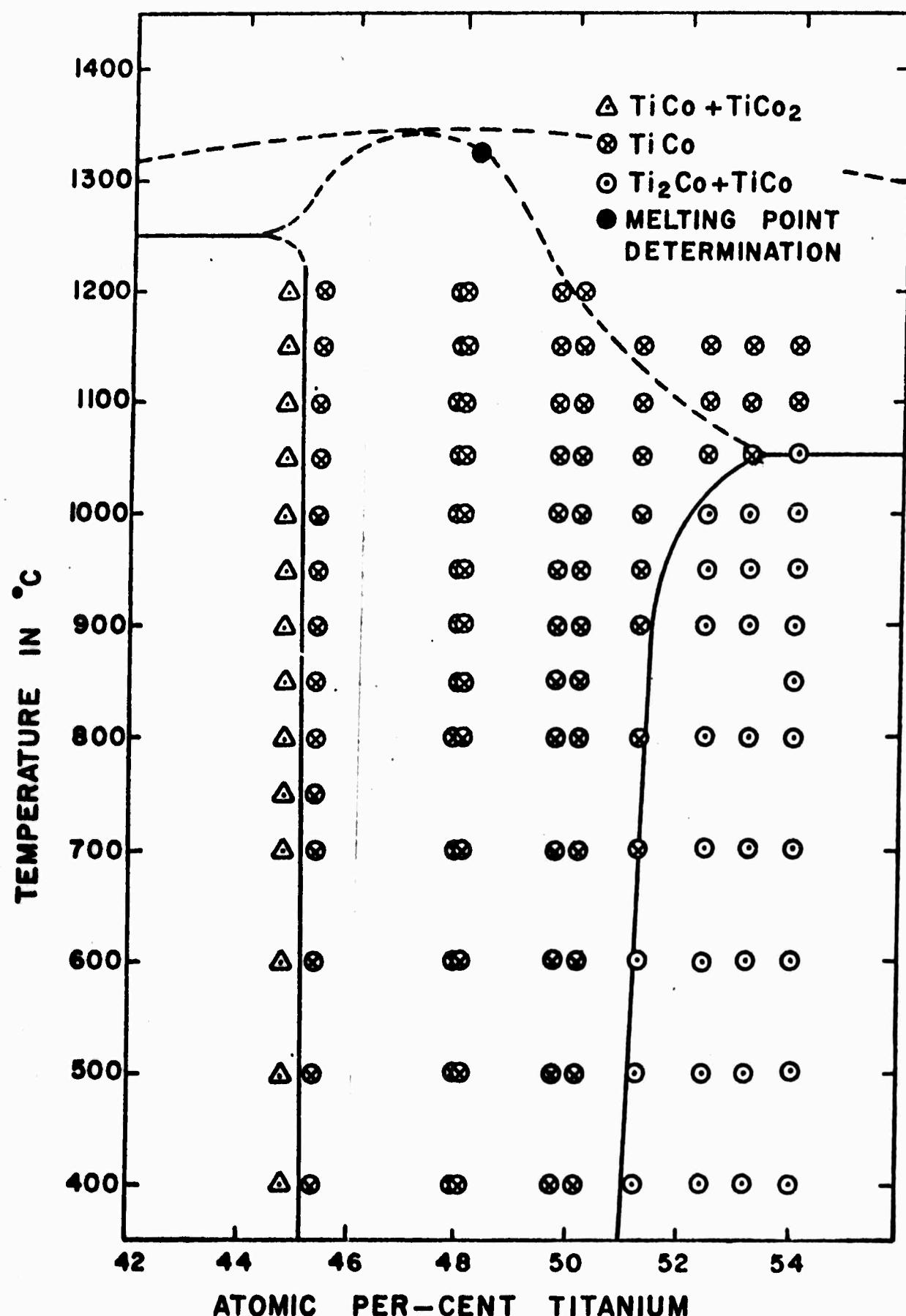


Fig. 1 - PHASE RELATIONSHIPS NEAR THE EQUIATOMIC COMPOSITION AS ESTABLISHED BY HIGH TEMPERATURE X-RAY DIFRACTOMETRY.

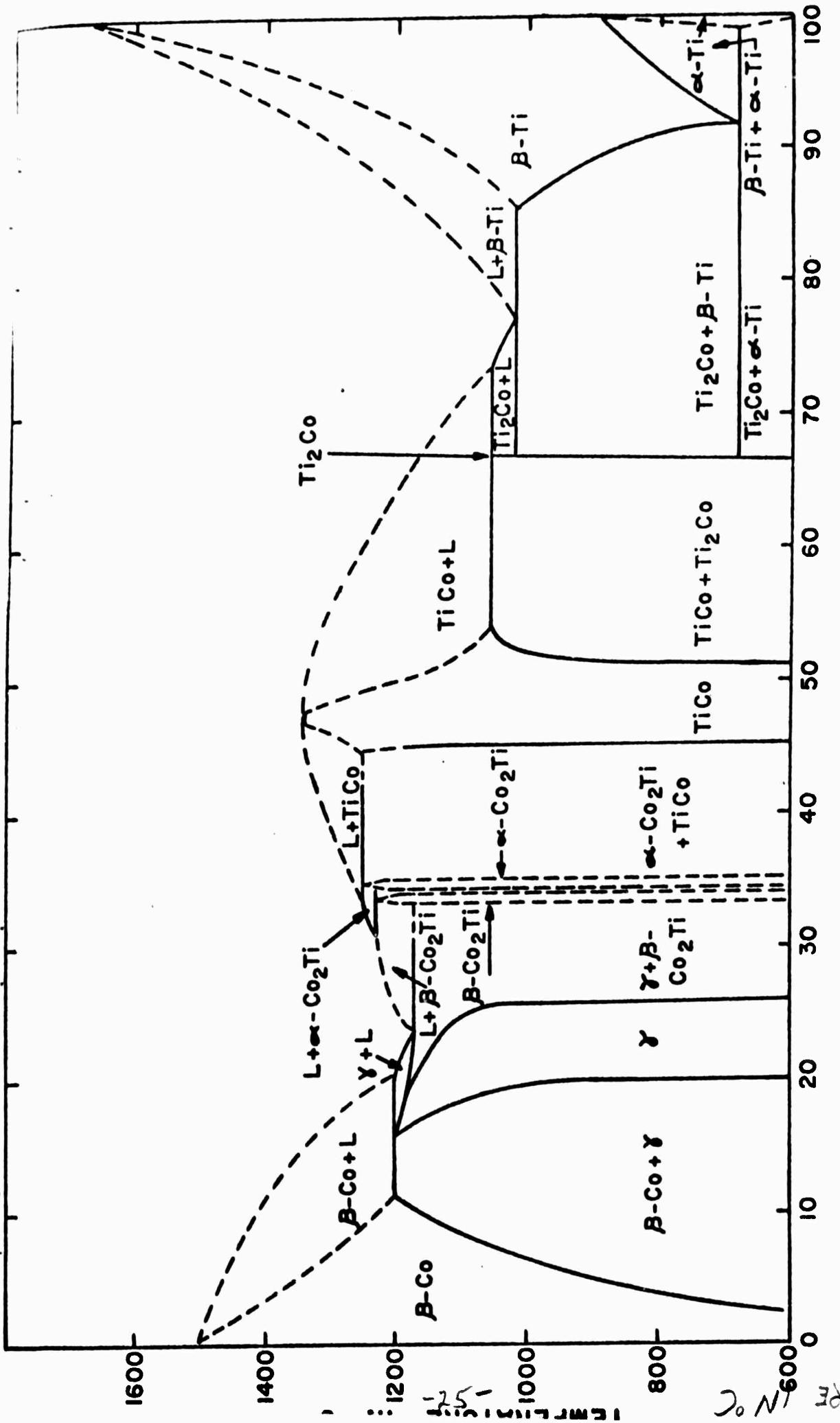


FIG. 2 - THE PROPOSED TITANIUM - COBALT PHASE DIAGRAM.

TEMPERATURE T IN $^{\circ}\text{C}$

PART III

UNPUBLISHED WORK

PREPARATION OF VOLATILE COMPOUNDS

Many compounds do not lend themselves to preparation by electron beam zone refinement due to their tendency to decompose in vacuum. Likewise some metals, e.g. chromium, because of their high vapor pressure, are difficult to process in the high vacuum used in electron beam zone refinement. Therefore, a technique was sought that would permit zone melting under high pressures of inert gases.

A. Furnace Design -

The high frequency furnace which consisted of a work coil embedded in a refractory cement surrounded by a water-cooled Niron 52 magnetic shield, is depicted in Fig. 1. This high magnetic permeability shield served to localize the field of the work coil and to prevent electromagnetic coupling and subsequent heating of the scanning assembly. The water-cooling for this shield was provided by diverting, through insulation nylon spacers, some of the water flowing through the coaxial power input. This arrangement precluded the necessity of providing additional water feed-throughs. Two furnaces were built having the above design but differing in load coil type. The first had a load coil consisting of thirteen turns of 1/8" O.D. copper tubing. This load coil was found to be very efficient. However, it had the shortcoming of overheating and failing due to insufficient water flow when crucible temperatures reached $\sim 1800^{\circ}\text{C}$. The second

copper tubing and was found to be entirely satisfactory at crucible temperatures in excess of 2100°C.

B. Furnace Calibration -

The II-VI compounds will decompose quite readily despite high autoclave pressures if the melting point is exceeded by a large margin. The successful melting of these compounds therefore necessitated that a precise knowledge of the temperature generated in the furnace be obtained. The use of a thermocouple in this apparatus was found to be impractical because the melting points exceed the limits of most practical thermocouples, and because the motion of the crucible necessitated that the thermocouple be attached to the high frequency furnace where electromagnetic coupling frequently caused difficulties. It was therefore decided to calibrate the furnace for a fixed crucible dimension by placing a dummy crucible containing a thermocouple into the work coil and examining the variation of temperature as a function of the square of the current in the work coil. In a case of fixed coil and crucible dimension, the power dissipated in the crucible is directly proportional to this quantity. Therefore, if the rate of heat loss is a constant over the temperature range of interest, then one would expect a linear relationship between I^2 and crucible temperature. This linear relationship was found to exist at crucible temperatures above 1100°C. It was therefore found very

convenient to utilize the known work coil current to arrive at the melt temperature. Further calibration points were obtained from the melting points of materials such as ZnS, thus allowing for a calibration up to $\sim 2000^{\circ}\text{C}$. Using this arrangement, it was found that melting could be controlled to a degree which was entirely sufficient to prevent decomposition of the two sulphides studied.

C. Crucible Preparation and Design -

The crucibles used for both the CdS and ZnS studies were machined from a high purity graphite. The internal surfaces of all the crucibles were carefully polished and the crucibles degassed by heating to 1900°C in water. Two graphite crucible configurations were employed as depicted in Figure 2. The configuration of Figure 2a was the initial type used. However, it was found that this configuration did not lend itself to single crystal growth and therefore the second configuration, depicted in Figure 2b, was employed. As may be observed from the figure, the second configuration made use of a seed well $1/8$ " in diameter and $3/4$ " deep.

D. Operation -

CdS and ZnS pellets were prepared by compressing the charge in a powder compaction die. The resulting pellets were placed in a cylindrical, high purity, degassed graphite crucible approximately seven inches long. This crucible

served both to support the molten zone and to act as a susceptor to permit efficient inductive coupling to the charge. The crucible and its contents were then mounted on the scanning assembly, described in a previous report, which then permitted the entire crucible to slowly travel through the high frequency furnace depicted in Figure 1. The scanning assembly and the coaxial power input were all mounted on one end plate of the autoclave. Thus the furnace which is directly connected to the coaxial power input, could be aligned with respect to the scanning assembly and crucible prior to being enclosed in the autoclave. When the furnace was properly aligned and the travel of scanning assembly checked out, the entire assembly was installed into the autoclave which was then evacuated and flushed with the gas of interest several times, and then filled to a pressure of 1500 psi. For these studies, both argon and nitrogen were used in the autoclave. The charge was zone melted by passing a 450 kc/sec current from a 15 kw Lepel generator through the work coil in the high frequency furnace. When sufficient time had elapsed for the formation of the molten zone, which was approximately 1" long, the scanning assembly was activated and the refinement operation begun. Because of the exploratory nature of these studies, the number of zone passes was restricted to two.

Results on CdS and ZnS -

The early attempts at zone melting cadmium sulphide produced polycrystalline ingots which were fully dense but rather badly cracked. In an effort to correct this undesirable effect, the rate of scanning was reduced and crucibles of the type depicted in Figure 2b were employed. Using such a design, an experiment was conducted in which the scanning rate was 0.65 in./hr. over the seed length and 1 in./hr. over the remaining length. The resulting ingot shown in Figure 3 was monocrystalline over the seed length but became polycrystalline when the scanning rate was increased. Cracking was still evident but only to a very minor extent.

The CdS used in these studies was of an impure grade and it was thus quite surprising when the single crystal seed was observed to have a pale amber color of pure cadmium sulphide. It would appear that zone melting has the possibility of becoming a very effective means of producing high purity cadmium sulphide. These observations however result from visible observation and have not yet been confirmed by analysis.

Only one run was conducted upon ZnS and this resulted in a dense polycrystalline ingot which was free of cracks but gave evidence of incomplete melting.

Float-Zone Refinement of Chromium -

From the above results it became evident that zone refinement in a crucible is possible with CdS and most probably is also possible with ZnS. However, the greatest enhancement in purity is still achieved when a crucible-free system of zone refinement is utilized. It was for this reason that the initial attempts at float-zone refinement were undertaken of high vapor pressure metals. Nickel and chromium were selected, nickel because of availability and chromium because it is a technologically important metal of which single crystals have not been prepared and because of its high vapor pressure.

Both nickel and chromium have been successfully float-zone melted in the bomb zone refiner. In the case of chromium, it was found to use a pressure of less than 300 psi to prevent oxidation of the metal even though extreme care was taken to purify the argon gas used in the chamber.

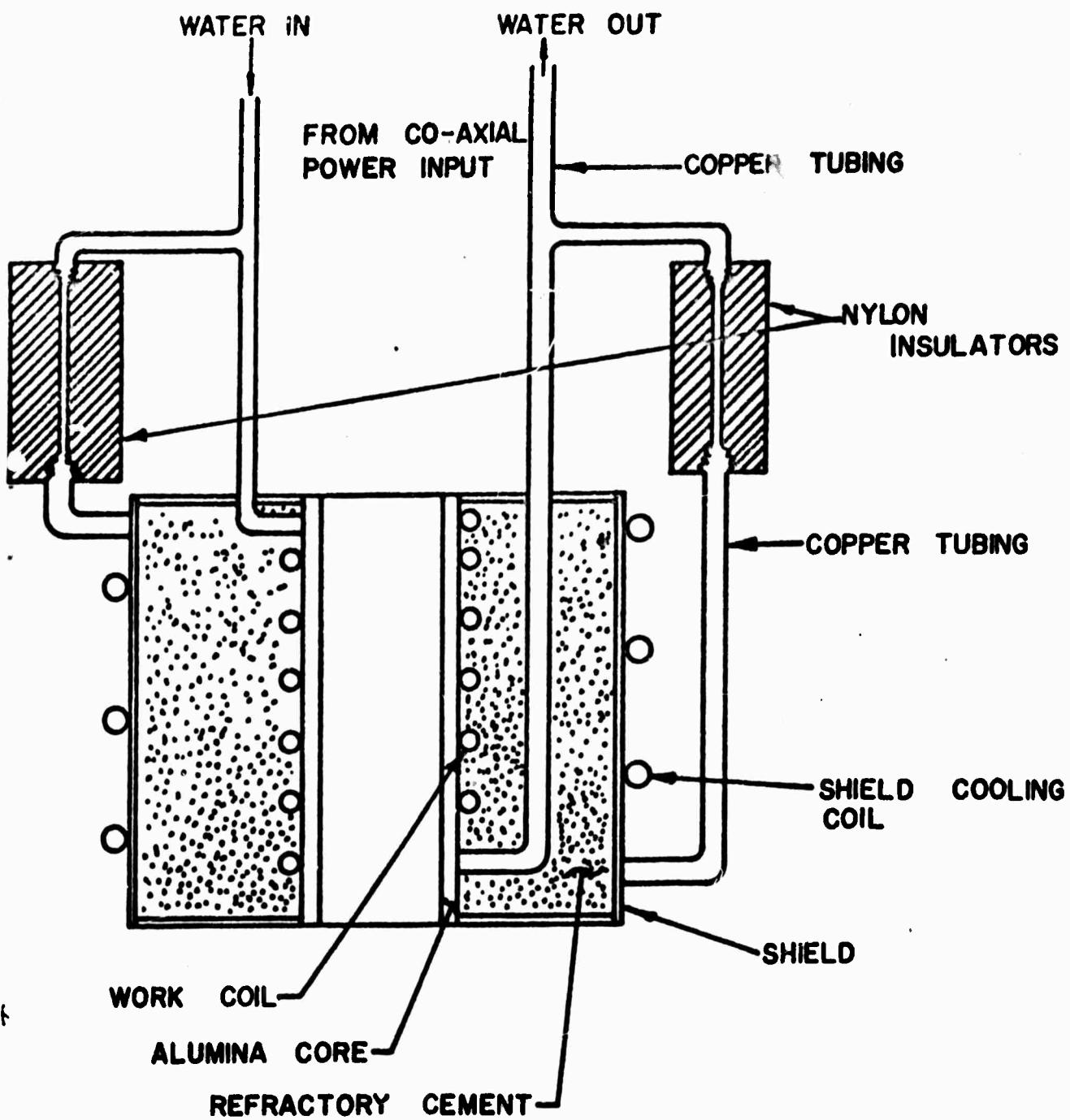
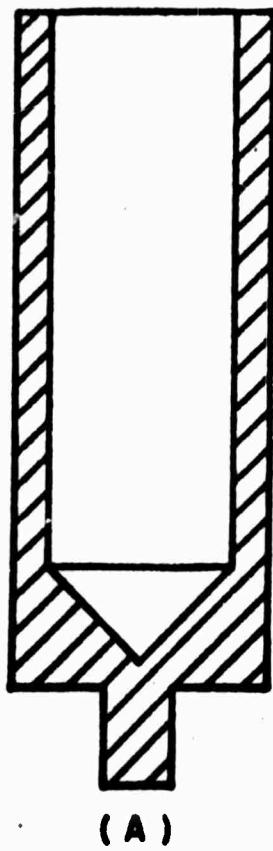
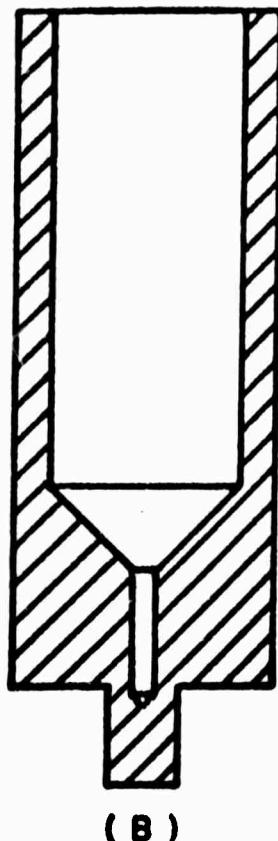


FIG. I CROSS SECTION OF HIGH FREQUENCY
FURNACE USED IN THE AUTOCLAVE.



(A)



(B)

FIG. 2 CROSS SECTIONAL VIEW OF THE CRUCIBLE CONFIGURATIONS USED IN MELTING CdS AND ZnS.

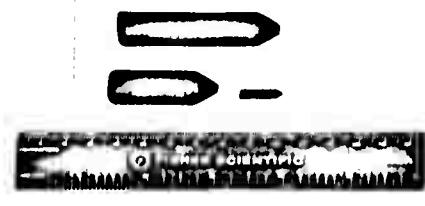


Figure 3 - Bomb Zone Refined Cadmium Sulphide

PREPARATION OF A CADMIUM-ALUMINA-SILICA GLASS

Infrared windows used in military applications are often exposed to severe environments such as high temperature, high humidity, abrading dust, etc. As a result, the materials which are used in these windows must also have in addition to the necessary optical properties, superior mechanical and thermal properties. A new glass, cadmium-alumina-silica, which transmits radiation from 0.5 to 5.0 microns, and which possesses very durable mechanical and thermal properties, is described.

Glass Preparation Techniques -

The glass which was studied in this investigation was composed of 63% CdO, 10% Al₂O₃ and 27% SiO₂. In order to prepare the glass, a charge of mullite, cadmium oxide and alumina and/or silica, was melted in a rotating platinum crucible under oxidizing conditions. The melting times were 30-60 minutes at temperatures from 1200°-1350°C.

The molten glass was poured into graphite and stainless steel molds which were pre-heated to 500°-600°C and cooled to room temperature at about 100°C/hr. The glass which was produced in the above manner, although containing some striations, was remarkably free of bubbles. Attempts are being made to eliminate the striations by more effective stirring of the melt, by increasing the melting time, and by increasing the pre-heat temperature of the molds.

Optical and Physical Properties -

(1) Transmission: Figure 2 is a plot of porcent transmission of normal incidence radiation as a function of wavelength for samples of different thicknesses. The 10% transmission values are seen to occur at 0.5 to 4.9 microns for a sample 2 mm thick. The percent transmission was probably lowered by the residual striations in the glass. As will be shown in the next section, reflections should account for only a 12% loss of the incident intensity, leading one to expect a maximum transmission of 85% through thin samples.

The transmission spectra shown here also exhibit water absorption bands at 2.8 microns. It has been shown (1) in similar glasses that melting the glass in vacuum eliminated the water bands. It has been suggested that this be attempted for the present glass.

(2) Index of Refraction: The index of refraction was determined by an image displacement technique to be about 1.70 at 0.5890 microns. If the index has an average variation with wavelength, it can be estimated to be 1.65 at 2 microns. The reflection from one surface can be calculated from

$$R = \frac{(n - 1)^2}{(n + 1)^2}$$

to be 0.06 of the normal incidence light of 2 micron wavelength. One would expect, therefore, only about 12% reflection

loss from the window, and, as a result, the anti-reflection coatings which are often needed for high index polycrystalline and single crystal materials, are not needed for this window.

(3) Hardness: The Knoop hardness of the glass was found to be 525 under a 100 gm load and is compared in Table I with values for other infrared transmitting materials. It is noteworthy that the cadmium-alumina-silica glass has a hardness value which allows it to be easily polished by conventional glass techniques in either flat or curved form without the difficulties sometimes encountered in polishing larger sapphire windows.

(4) Humidity Resistance: No detectable change was noted in optical properties of glass after three-day immersion in 25°C water. It is interesting to compare this behavior with that of a calcium-aluminate glass for which a polished surface is destroyed after one hour of water immersion (2).

(5) Thermal Expansion and Deformation Temperature: The average linear expansion coefficient of the cadmium-alumina-silica glass was found to be 5.0×10^{-6} in./in. $^{\circ}$ C over the temperature interval 25°-600°C. The measurements were made using a quartz tube dilatometer with dial gauge indicator as described in ASTM Standard C 337-57. Figure 3 is a plot of the linear expansion of the glass from 25° to 700°C. Although deformation temperatures are usually determined from interferometric dilatometer measurements, an

TABLE I
KNOOP HARDNESS OF INFRARED TRANSMITTING MATERIALS

<u>Type</u>	<u>Hardness</u>
A. GLASSES	
Fused Silica	470
Arsenic Trisulfide	109
Calcium Aluminate (Bausch & Lomb)	594
Typical Optical Crown	460
Typical Optical Flint	360
B. POLYCRYSTALLINE MATERIALS	
ZnSe (Irtran 4)	150
CaF ₂ (Irtran 3)	200
ZnS (Irtran 2)	354
MgF ₂ (Irtran 1)	576
MgO (Irtran 5)	640
C. SINGLE CRYSTALS	
Alkali Halides	<100
TiO ₂	880
Si	1150
Al ₂ O ₃	1370-2000

effective deformation temperature can be determined from the ASTM test. For the cadmium-alumina-silica glass the effective deformation temperature was found to be 650°C.

The value of the expansion coefficient is such that it should be possible to make glass-to-metal matched-expansion seals to a number of commercial iron-nickel alloys such as Carpenter Low Expansion "49" alloy.

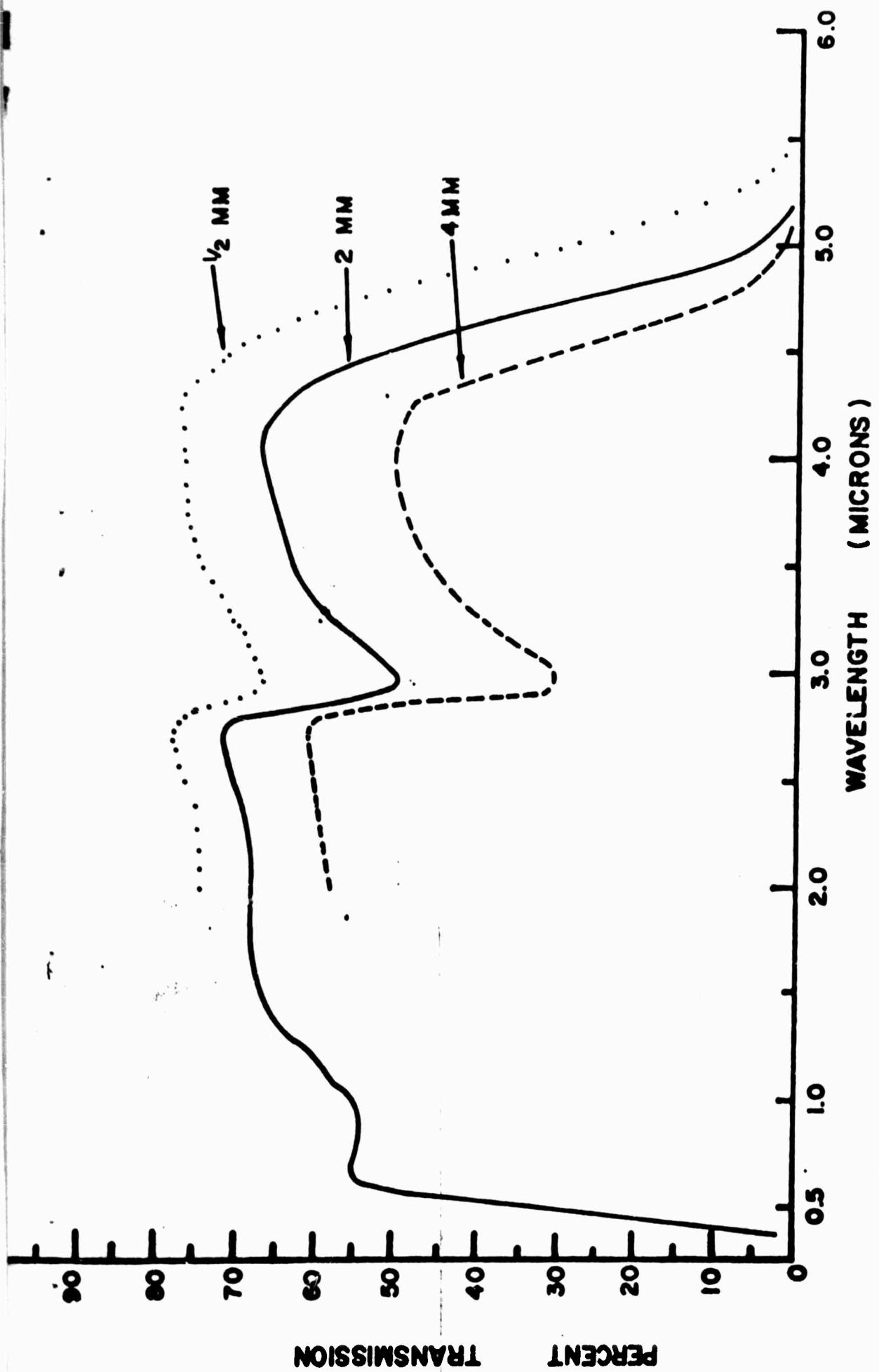
(6) Sag Temperature and Devitrification Temperature: The sag temperature of the glass was determined by a method described by Spinner, Cleek and Hamilton (3), in which a fiber of the glass 0.3 to 0.6 mm in diameter was supported at approximately 1/2" intervals on a platinum holder and placed on a known temperature gradient for 20 to 30 minutes. From the position at which the fiber sagged between supports, a sag temperature could be determined to $\pm 10^{\circ}\text{C}$. For the cadmium-alumina-silica glass the sag temperature was found to be 660°C.

In addition to determining the sag point, the above technique can also give an indication of the tendency of the glass to devitrify upon annealing. In this case, the beginning of devitrification was observed in the glass at 710°C. Although this temperature is above the annealing range, it should be noted that increasing the time at temperature will decrease the temperature at which devitrification occurs.

All the optical and physical properties presented in this section are listed for ready reference in Table II on the following page.

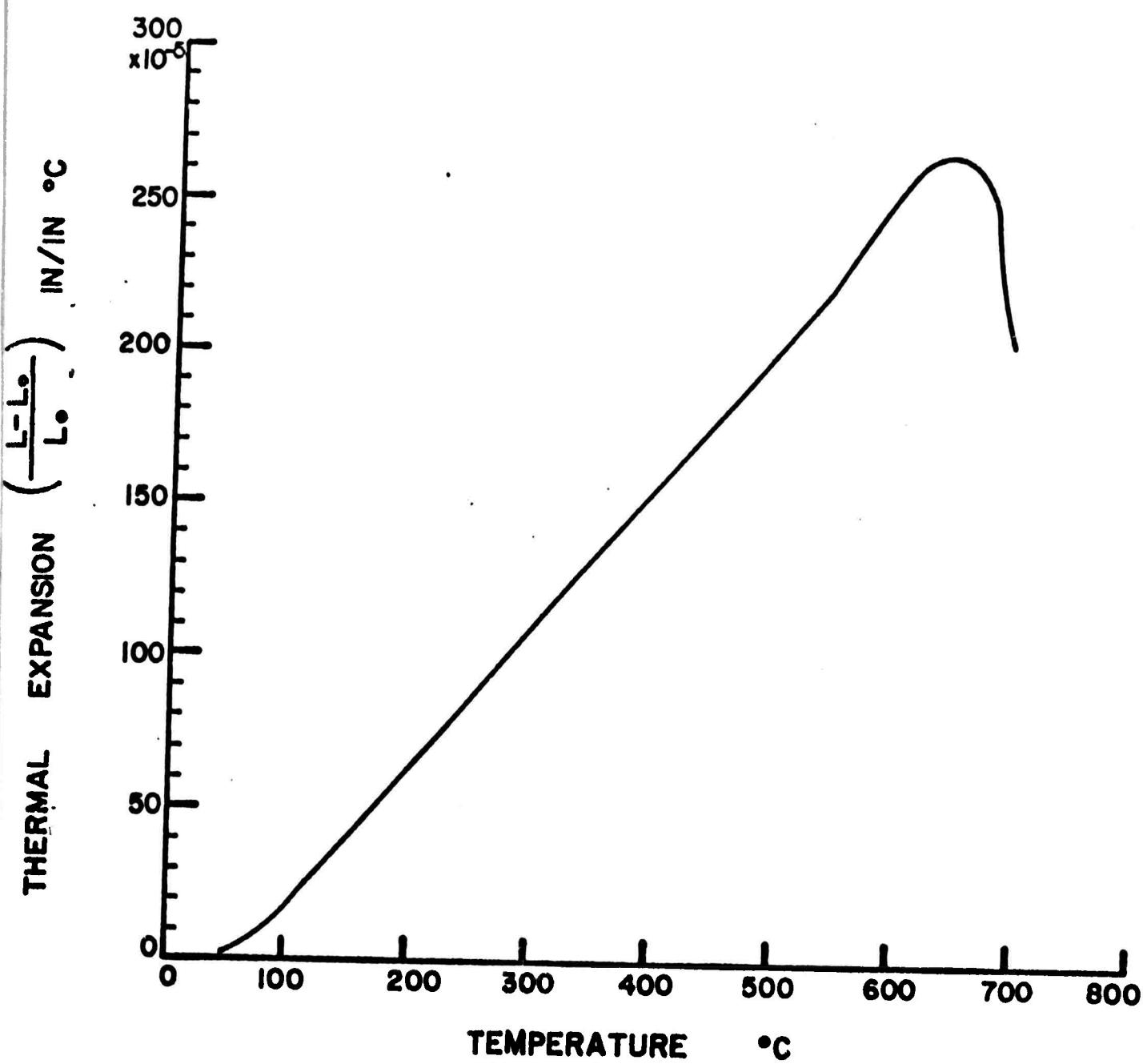
TABLE II
PROPERTIES OF CADMIUM-ALUMINA-SILICA GLASS

1. Transmission Range:	0.5-4.9 microns 10% transmission points for 2 mm sample.
2. Index of Refraction:	1.70 N _D
3. Hardness:	525 Knoop 100 gm Load
4. Thermal Expansion 25° - 600°C:	5.0 x 10 ⁻⁶ in./in.°C
5. Sag Point:	660°C
6. Deformation Point:	650°C
7. Devitrification Temperature of Glass Fiber:	710°C
8. Effect of Water Immersion (72 hours at 25°C)	NONE
9. Density:	4.43 gm/cm ³



OPTICAL TRANSMISSION OF CADMIUM- ALUMINA- SILICA GLASS

Figure 2



THERMAL EXPANSION OF CADMIUM- ALUMINA- SILICA
GLASS

Figure 3

-17-

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CHARACTERIZATION BY FIELD ION MICROSCOPY

The field ion microscope is capable of producing high contrast images of specimens at magnifications over one million diameters with a resolution of three angstrom units. With this magnification and resolution, it is possible to distinguish individual atoms on the surface of the specimen under examination and thereby study surface structure and solute content on an atomic scale. Although only surface atoms are imaged in the field ion microscope, it is possible to study bulk effects by successively removing surface layers of the specimen by controlled electric field evaporation. In this manner, it is possible to study long and short range ordering, solute clustering, vacancy-interstitial complexing, radiation damage, etc.

Tungsten filaments of commercial purity have been successfully imaged in the field ion microscope. As shown in Figure 1 individual tungsten atom positions were clearly revealed, but of more importance, impurity atoms were also observed and easily distinguished from those of the host lattice. Although the identity of the impurity atoms is unknown, attempts are now being made to image ultra-high purity zone refined tungsten for comparison purposes. Some problems are being encountered in reducing the ultra-high purity rod to the required filament size without contamination.

Figure 1

**Field Ion Microscope - Photograph of
Surface Atoms of Tungsten Needle**

**Magnification: approaching 1,000,000
diameters**

ELECTROTRANSPORT AS A MEANS OF PURIFICATION

An apparatus was constructed which allowed heavy currents to be passed through a metal rod while it was maintained in a vacuum or inert atmosphere and its ends were kept near room temperature by water cooling. This apparatus has been used to study the possibility of using the electrotransport phenomenon for the further purification of electron beam zone refined iron.

A series of iron rods each 6 inches in length and 0.090 inch in diameter was prepared from a single specimen of electron beam zone refined iron which contained a total impurity content of about 50 ppm. A direct current of 70 amps was passed through each of three of the specimens for a period of 72 hours. During this period the specimen was maintained in an atmosphere of pure hydrogen and, as a result of Joule heating, its midpoint was at a temperature of about 1300°C. Similar experiments were carried out on two further specimens using alternating instead of direct current.

The impurity distribution along the lengths of each of these five specimens was examined by making resistance ratio measurements. By comparing the results from the D.C. and A.C. experiments it was possible to separate out effects due to the Soret effect from those due to electrotransport. In this way it was found that in the D.C. experiments electrotransport

had caused a measurable movement of impurities away from the anode. This effect was, however, small compared to the Soret diffusion which accompanied it. These results are therefore discouraging from the point of view of developing a purification technique, but further work will be required to establish the effects of current density and temperature on the magnitude of the phenomenon before the method can be rejected.

The behavior of the impurity distributions in the five rods on annealing was studied by repeating the resistance ratio measurements after successive two hour vacuum annealing treatments at 200°, 350°, 450° and 650°C. Annealing at 200°C produced an overall increase in the resistance ratios and this was not significantly altered by the 350° and 450°C anneals. The 650°C anneal, however, produced an overall decrease in the resistance ratios of about the same magnitude.

CHARACTERIZATION OF Ni₃Al

In the course of a study on the preparation of intermetallic compounds, a high propensity of twins was observed in recrystallized Ni₃Al. This compound has the ordered Cu₃Au structure. It was decided to determine the crystallography of these twins by x-ray diffraction techniques.

The compound was prepared by arc melting appropriate quantities of nickel and aluminum. The resulting rod was then electron beam zone leveled, swaged to about 40% R.A. and recrystallized by annealing for five hours at 1300°C. A high density of annealing twins was observed in metallographic samples of the recrystallized material. The x-ray data obtained thus far indicate that these twins are similar to the annealing twins found in f.c.c. metals.